Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 854

Neutral to Alkaline Rosin Sizing Using
Polyethyleneimine-epichlorohydrin (PEI-epi) as a Mordant

Y. Xu, B. Hartong, and Y. Deng

May 2000

Submitted to
Journal of Applied Polymer Science

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 52 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

Neutral to alkaline rosin sizing using polyethyleneimine-epichlorohydrin(PEI-epi) as a mordant

Yufeng Xu, Bradley Hartong, and Yulin Deng*
Institute of Paper Science and Technology, 500 10th Street N.W., Atlanta, GA 30318

INTRODUCTION

Rosin with alum has been used traditionally in the paper industry to improve the water resistance of paper. Because of the well-known pH requirement of alum, the system was effective only in an acidic papermaking process. In recent years, papermaking conditions have been rapidly shifting from acidic to neutral-alkaline because of lower cost, higher paper strength, less corrosion, and increased productivity. This, in turn, results in the shift of internal sizing agent from rosin-alum to synthetic or cellulose-reactive agents such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA).

Though effective, AKD and ASA are more expensive than rosin size. Other disadvantages include hydrolysis and deposition of these sizing agents, paper-surface slipperiness, and sizing reverse when calcium carbonate is involved. Papermakers have continued to seek novel and effective sizing methods. Because of the low price and similar chemistry, rosin-based sizing at neutral or alkaline pH has received increasing attention. One critical step in this trend is to find a stable mordant at higher pH to substitute for alum. Two promising classes of chemicals studied to date are polyaluminium chloride (PAC) and polyamines. Wortley [1] found that replacing alum with PAC increased the efficiency of rosin sizing significantly at pH above 5.5. Similar work was also done by Liu [2, 3] and Colasurdo [4]. Biermann [5] and Wu et al. [6] reported that polyamines could be used to improve rosin-sizing efficiency in neutral to alkaline conditions. Among the polyamines they studied, the polyallylamine is the best.

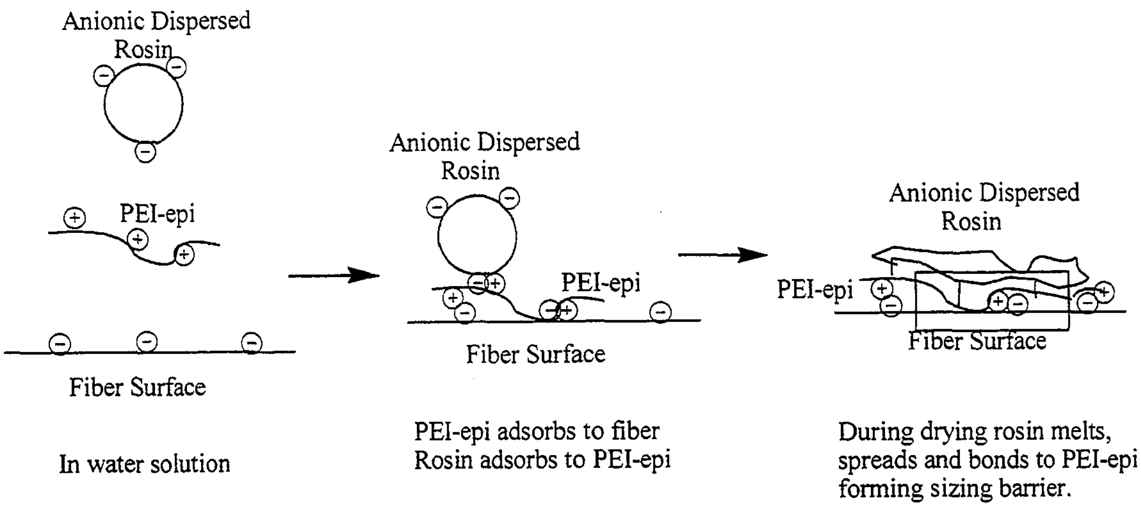
* Author to whom correspondence should be addressed.

Other polyamines, such as polyethyleneimine (PEI), polyvinylamine, and poly(dimethylaminoethyl methacrylate), also improved rosin-sizing efficiency. They concluded that the presence of protonated amines in the polymer chain is important. They also found that primary amines (-NH_2) are the best, secondary amines (-NH-) have only marginal effect, and quaternary amines do not contribute to the rosin-sizing development. Zhang and Biermann [7] also studied the combination of PEI and metal ions and found that Fe^{2+}/PEI is very effective at pH below 7 and Cu^{2+}/PEI is effective up to a pH of 9. They concluded that polyamines can improve the rosin-sizing efficiency by the formation of the complex between the mordants (polyamines or metal ions) and rosin molecules.

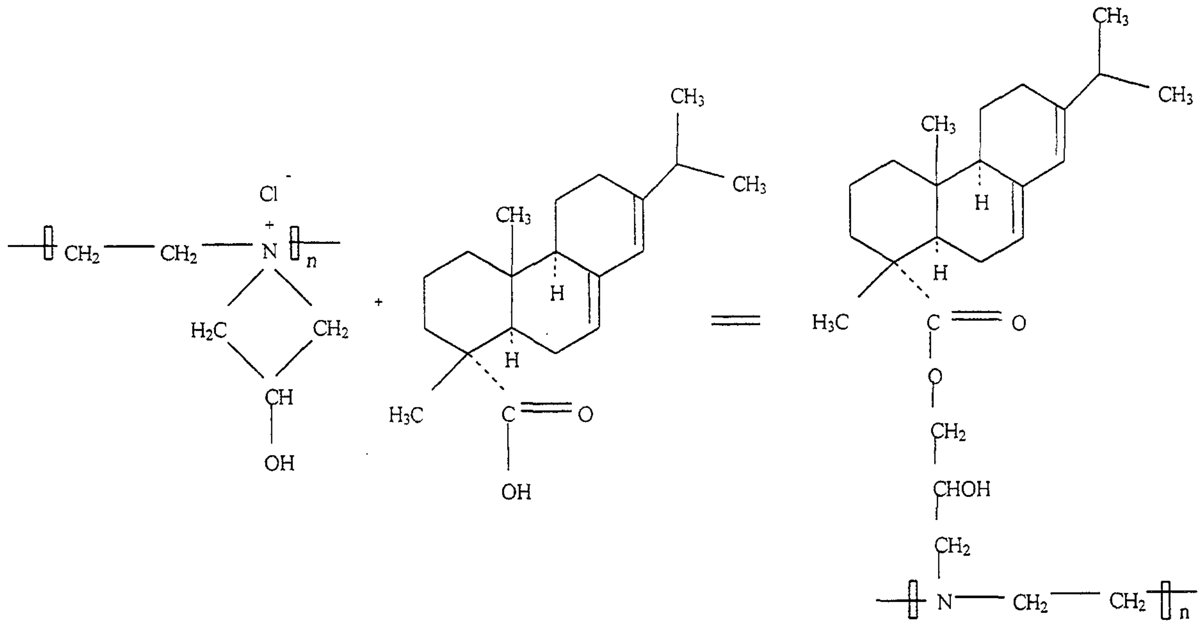
Isogai [8] and Kitaoka et al. [9] studied systems of cationic emulsion of fatty acid anhydrides in the presence of polyamideamine-epichlorohydrin resin. Isogai indicated that although polyamideamine-epichlorohydrin resin can form a chemical bond with fatty acid, this reaction did not contribute to the sizing. He further concluded that the chemical bond between sizing agent and fiber surface groups is not an important factor for sizing development. In other studies [10-11] including the systems of rosin-alum sizing, AKD, and ASA, similar conclusions were reached.

In the work described below, polyethyleneimine-epichlorohydrin (PEI-epi) was used as an anchoring aid for rosin. A similar class of polymer, epoxidized polyamide, has also been widely used in the paper industry to improve the wet strength of paper products. This class of wet-strength resin is normally referred to as poly(aminoamide)-epichlorohydrin (PAE) resin or polyamide-polyamine-epichlorohydrin (PPE) resin. The wet-strength mechanism is generally believed to be that the pendent azetidinium group on the polymer reacts with the amine groups of other resin molecules or available carboxyl groups in the paper to give a crosslinked network. Because rosin contains multiple carboxyl groups, it is possible that a covalent bond will form between rosin and PEI-epi. Although Isogai's studies showed that no chemical bonds were formed between sizing agents and fibers, there are still many arguments in this area [12-15]. Furthermore, in Isogai's studies, the paper sheets were dried at 20 °C before curing. The air-dry process may affect the chemical-bond formation in the post curing process because the molecules cannot move and react with each other if no water is present. Therefore, further study is necessary to determine the contribution of chemical bonding in the sizing development. This study showed that PEI-epi can significantly improve rosin sizing efficiency in neutral and alkaline conditions, results that differ from those reported by Isogai [8, 9].

Because of the special structure of PEI-epi, this chemical can react chemically or electrostatically with both fiber and rosin. The anchoring of rosin on fiber through PEI-epi is illustrated in Scheme 1 and the possible chemical reaction is given in Scheme 2.



Scheme 1. A possible mechanism for PEI-epi/dispersed rosin sizing (top). An enlargement of the box area shown in Scheme 2 gives possible chemical bonds formed in this process.



Scheme 2. Projected reaction between rosin and PEI-epi.

EXPERIMENTAL

A commercial bleached kraft pulp was used in the experiments. The pulp was obtained in dry-lap form. After soaking overnight, the pulp was beaten to a Canadian Standard Freeness (CSF) of 500 in a Vally beater. PEI-epi was synthesized in the laboratory by reacting epichlorohydrin (Aldrich) with PEI (BASE product, 35% solid content). Procedures for PEI-epi synthesis are as follows. To 100 ml 5% PEI that had been cooled to a temperature of 5°C in an ice bath, a prescribed amount of epichlorohydrin was added slowly. The amount of epichlorohydrin was determined according to a desired substitution ratio of 1:1. The mixture was then returned to room temperature (25 °C) in about 2 h. The reaction continued for another 4 h with stirring. Hydrochloric acid was then added to adjust the pH to 4. The finished product was diluted to a concentration of 5% and refrigerated for later use. Anionic rosin emulsion and rosin soap were provided by Eka Nobel Inc.

Stock pH was adjusted to the target pH before the mordant was added. After mixing a few seconds, the required rosin was added to the stock and mixed again for a specified time. A prescribed amount of stock was then added to a handsheet mold to make handsheet, which were pressed for four min and then dried on a drum drier at 115°C-120°C for 4 min. The Hercules sizing test (HST) was conducted 2 h after drying using 1% formic acid ink.

RESULTS & DISCUSSION

Effect of major variables on sizing

A 3^3 experimental design was run to determine the effects of variation in rosin concentration, rosin-to-polymer ratio, and reaction time of rosin with PEI-epi. A total of 27 experiments were run. The experimental conditions of different runs are given in Table 1. All of these experiments were conducted at room temperature and pH 8.1.

The experimental design tests showed that rosin concentration, reaction time, and rosin-to-polymer ratio had significant effects on the degree of sizing. Figures 1-3 show the value of each variable tested in the experimental design. Each value in Fig. 1-3 is the average of nine different experiments. For example, the HST value at 1% rosin in Fig.1 is the average result of all runs at 1% rosin amount in Table 1. The large difference between HST values (Fig. 1) illustrates that rosin concentration is by far the biggest factor in degree of sizing of the three factors studied in the design. The higher the rosin concentration, the better the sizing. Increasing the ratio of rosin to PEI-epi showed significant drops in HST values (Fig. 2). Within the ranges tested, a 1.2:1.0 weight ratio of rosin to polymer is the best. Though not shown in the figure, another run of experiments showed that reducing the rosin-to-polymer ratio to 1:1 also lowered the HST value. In addition, a low rosin-to-polymer ratio will not be economically feasible. Some sizing could be achieved at the 2.0:1.0 ratio and almost no sizing development was found at the 4.0:1.0 ratio. The drop in sizing as the PEI-epi dosage is decreased demonstrates that the PEI-epi is contributing to the sizing effect. The rosin reaction time had a smaller effect than the other two variables studied in the experimental design. Figure 3 shows that 10 min reaction time clearly provided the lowest HST values. The difference between a half minute and two minutes is not statistically significant, but the trend seems to indicate that a shorter time is better. Sizing results at the best rosin/PEI-epi ratio (1.2:1) and reaction time (0.5 min.), as well as different rosin levels are shown (Fig. 4).

Table 1. Experimental Conditions

Run Number	Rosin Amount, %	Rosin/PEI-epi Ratio	Reaction Time, min.
1	0.2	1.2	0.5
2	0.2	1.2	2
3	0.2	1.2	10
4	0.5	1.2	0.5
5	0.5	1.2	2
6	0.5	1.2	10
7	1.0	1.2	0.5
8	1.0	1.2	2
9	1.0	1.2	10
10	0.2	2.0	0.5
11	0.2	2.0	2
12	0.2	2.0	10
13	0.5	2.0	0.5
14	0.5	2.0	2
15	0.5	2.0	10
16	1.0	2.0	0.5
17	1.0	2.0	2
18	1.0	2.0	10
19	0.2	4.0	0.5
20	0.2	4.0	2
21	0.2	4.0	10
22	0.5	4.0	0.5
23	0.5	4.0	2
24	0.5	4.0	10
25	1.0	4.0	0.5
26	1.0	4.0	2
27	1.0	4.0	10

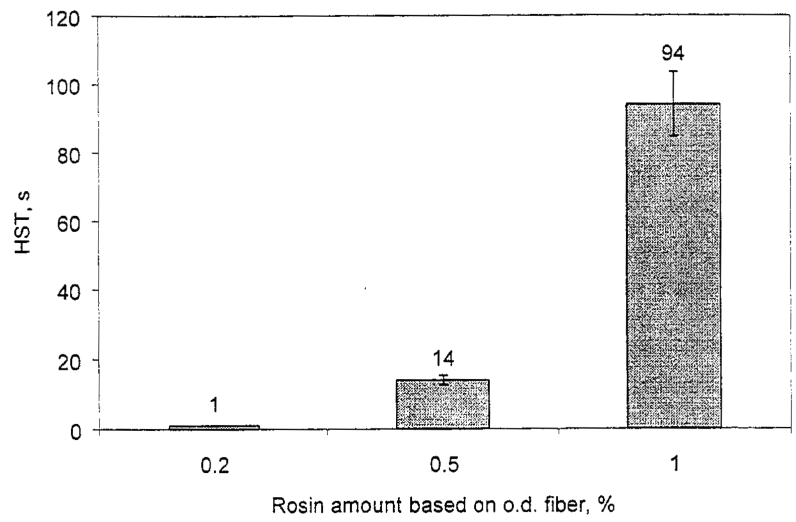


Figure 1. Effect of Rosin Amount on Sizing at pH 8.1

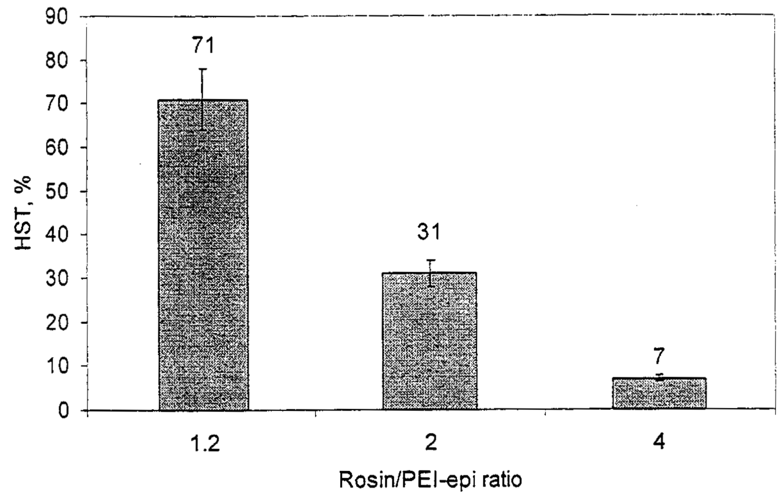


Figure 2. Effect of Rosin/PEI-epi Ratio on Sizing at pH 8.1

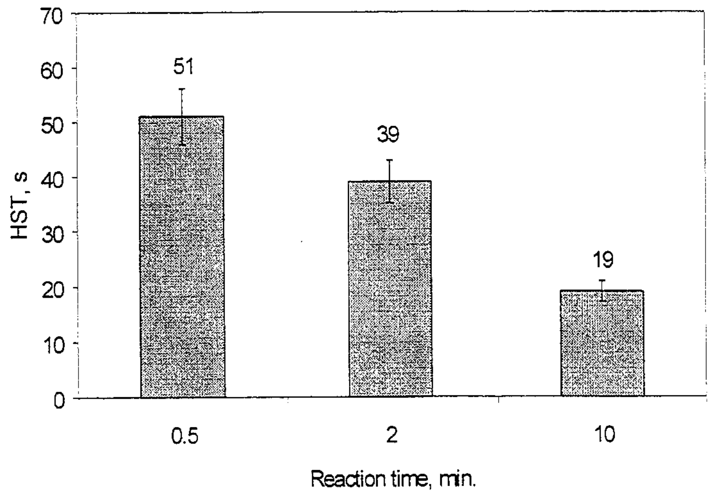


Figure 3. Effect of Reaction Time on Sizing at pH 8.1

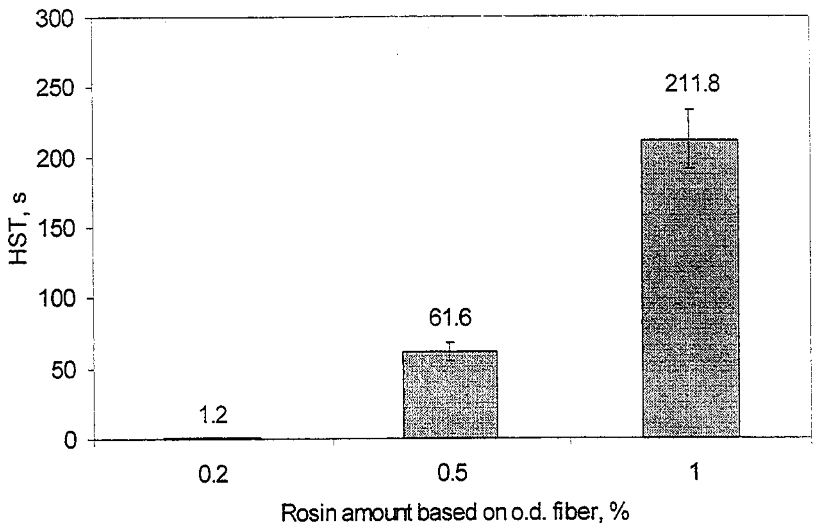


Figure 4. Sizing Results at Rosin/PEI-epi Ratio of 1.2, Reaction Time of 0.5 Second and pH 8.1

Effectiveness of PEI-epi/Dispersed Rosin Sizing at Other Conditions

Some effects of pH on PEI-epi/dispersed rosin are shown in Fig. 5. The pH results seem to indicate that PEI-epi/dispersed rosin sizing favors a neutral pH. The highest level of sizing occurred at a pH of 6.5. Sizing dropped off at a pH of 5.0. This is similar to the case of PAE resin in wet-strength application [16]. The reason for this pH effect is not clear. A tentative explanation is that fewer dissociated carboxyl groups on the fibers at low pH discourage the adsorption of positively charged PEI-epi or the complex of PEI-epi and rosin. The decline in sizing at high pH may be related to the self-crosslinking of PEI-epi or the saponification of rosin. It appears that PEI-epi/dispersed rosin sizing can provide significant levels of sizing within the pH range used for neutral to alkaline papermaking. It should be noted that even though the sizing efficiency dropped off above pH 6.5, the reasonable sizing (226 s of HST) was observed at pH 8.1. Even at pH 9.5, the HST value is still 108 s. It was reconfirmed in this study (not show here) that rosin alone or rosin/alum system cannot give remarkable sizing at pH higher than 8. The results shown in Fig. 5 indicated that rosin sizing efficiency at high pHs was significantly improved by adding PEI-epi. PEI-epi/dispersed rosin sizing appears to be adversely affected by high stock temperature. Figure 6 shows the effect of stock temperature on

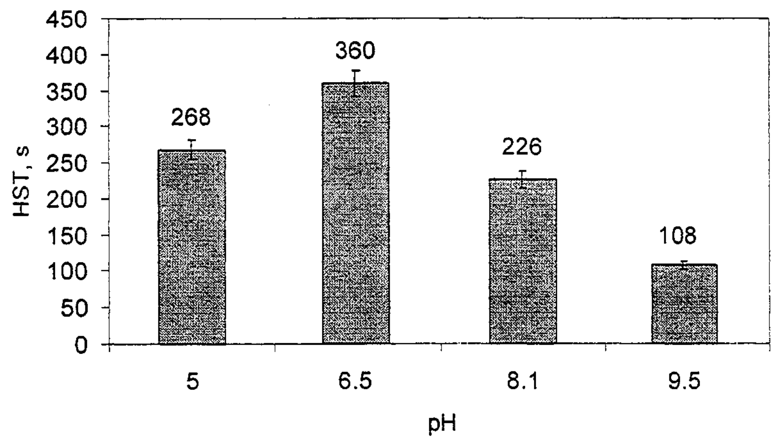


Figure 5. Effect of pH on Sizing
(Made at 1% rosin, rosin/PEI-epi=0.2, reaction time of 0.5 min)

HST. At 65^{O}C, the degree of sizing falls off significantly. A similar pattern is seen in alum-dispersed rosin sizing in acidic conditions [17].

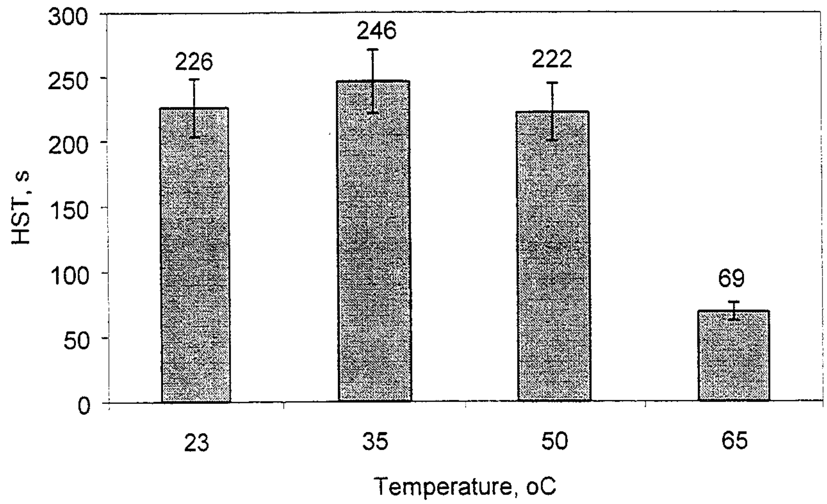


Figure 6. Effect of Stock Temperature on Sizing (Made at 1% rosin, rosin/PEI-epi=0.2, reaction time of 0.5 min and pH 8.1)

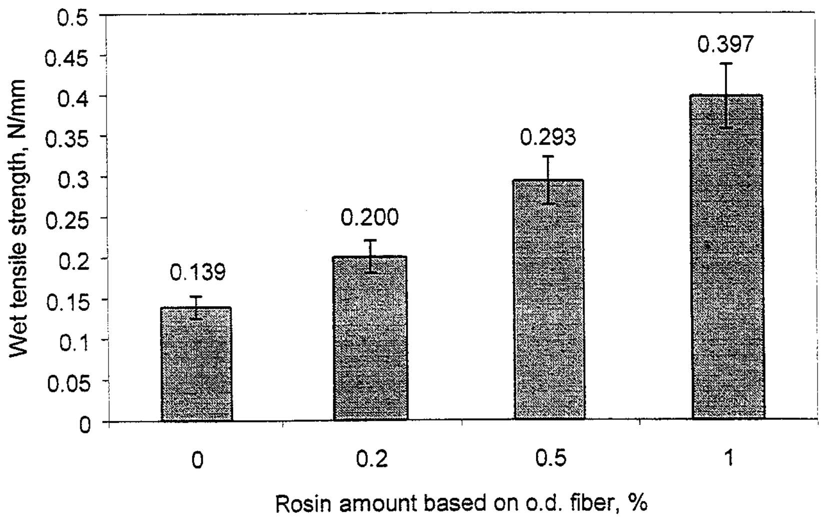


Figure 7. Tensile Strength of Rosin/PEI-epi Sized Paper (Made at 1% rosin, rosin/PEI-epi=0.2, reaction time of 0.5 min. and pH 8.1)

A side effect of using PEI-epi as a mordant of rosin sizing is the improvement in wet-tensile strength of sized paper. The wet-tensile loads of samples treated at different rosin levels are given in Fig. 7. The wet strength comes from azetidinium groups on PEI-epi that were not taken by rosin in the sizing process. These free groups will react either with the ammonium on another PEI-epi molecule to form self-crosslinking or with the carboxyl groups on the fiber to form co-crosslinking. This will be an additional advantage for paper grades in which some wet strength is desired.

Comparison of Rosin/PEI-epi Sizing to Traditional Rosin Sizing

Sizing using dispersed rosin and alum at acidic pH and rosin-soap sizing using PEI-epi as mordant at neutral pH were also conducted and the results are compared with that from dispersed rosin/ PEI-epi sizing discussed above. This allowed comparisons to be drawn based on production using the same lab equipment and conditions. As can be seen in Fig. 8, acid alum-dispersed rosin sizing at a pH of 4.8 gave similar degrees of

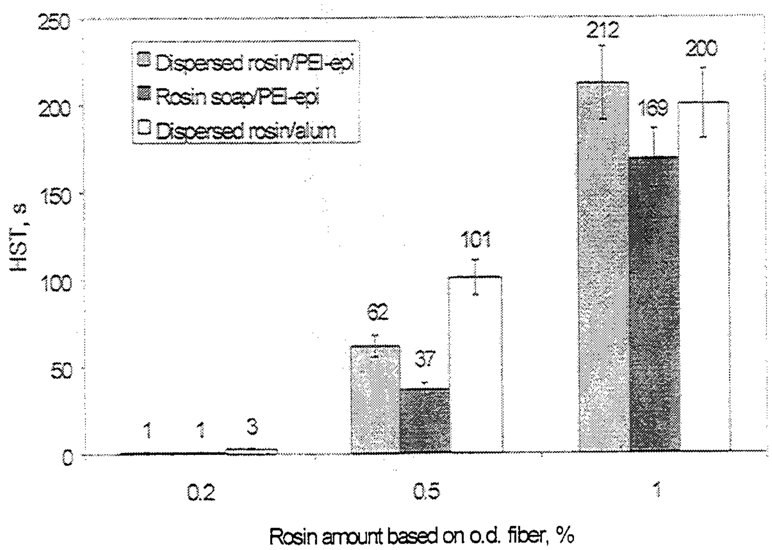


Figure 8. Rosin/PEI-epi Sizing vs. Rosin/alum Sizing (Rosin/PEI-epi: 1% rosin, rosin/PEI-epi=0.2, pH 8.1, 0.5 min. Rosin/alum: 1% rosin, rosin/alum=1:1, pH 4.8, 0.5 min.)

sizing to the dispersed rosin/PEI-epi sizing at a pH of 8.1. The rosin soap/PEI-epi provides a slightly lower degree of sizing than the dispersed rosin/PEI-epi and dispersed rosin/alum. These results suggest that the combination of PEI-epi and rosin can be potentially used as an alkaline-sizing additive.

PEI-epi/Dispersed Rosin Sizing Comparison of Bleached and Unbleached Pulp

PEI-epi/dispersed rosin sizing at different rosin dosages was also tested on unbleached pulp. The sizing level of unbleached pulp is not remarkable until a rosin dosage of 1 % is used. On the suspicion that anionic trash was causing the problem, the charge densities of the pulp filtrates were measured via colloid titration. It was found that the unbleached pulp had a cationic demand of 81 μeq/L while the bleached pulp had only a demand of 21 μeq/L.

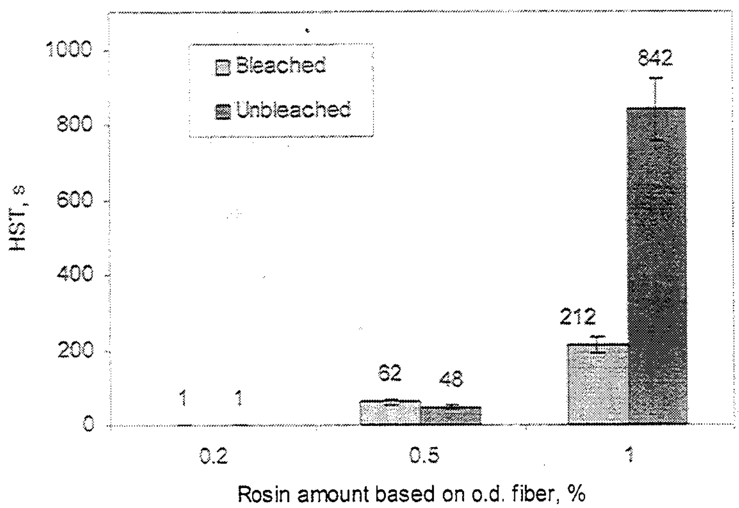


Figure 9. Comparison of Rosin/PEI-epi Sizing on Bleached and Unbleached Pulps (Made at rosin/PEI-epi=0.2, reaction time of 0.5 min and pH 8.1)

The unbleached sample was neutralized to 21 μeq/L cationic demand by adding polyDADMAC to get a more direct comparison to the bleached stock. The results of this comparison are shown in Fig. 9. The sizing level of unbleached pulp at a 0.5% rosin amount increased significantly to a level that is comparable to bleached pulp, while that of unbleached pulp at 1% rosin is several times higher than bleached pulp. It appears from these results that one of the factors affecting the performance of this dual-sizing system is the retention, which has a close relationship with the cationic demand. More research is needed for fully understanding of this typical system.

Possible Mechanism of PEI-epi/Dispersed Rosin System

Two possible ways for the PEI-epi to anchor rosin are through electrostatic force and/or covalent bond. The high charge density on PEI-epi is able to reverse the charge on the fiber surface from negative to positive and make the anionic rosin emulsion substantive to the fiber. On the other hand, the azetidinium group on PEI-epi has the potential to react with the carboxyl group on rosin to form a covalent ester bond.

To see if the electrostatic attraction is the sole reason for rosin anchoring, unmodified PEI was used instead of PEI-epi in the sizing process described above. PEI has the same backbone length as PEI-epi and colloid titration results showed that the charge density of PEI is higher than that of PEI-epi. The dosage range of PEI was thus chosen to cover the points of both equal weight percentage and equal charge density with PEI-epi based on the fiber weight. The results showed that at all levels of PEI used, almost no sizing was achieved when a unmodified PEI was used with dispersed rosin. This is a little different from Zhang and Biermann's report [7] in which they showed a small improvement on rosin sizing using PEI as a mordant. However, they also indicated that PEI alone is not an effective mordant for rosin-alkaline sizing. The little difference between Zhang and Biermann's results and ours using unmodified PEI should not be surprising because different pulps and conditions were used.

To understand the contribution of electrostatic force vs chemical reaction, similar sizing experiments were also run using polyDADMAC and rosin. As in the experiments with PEI alone, almost no sizing was seen. These results indicate that the charge on PEI-epi may not be the dominant contributor to the anchoring of rosin on fiber surface with a required orientation.

FTIR was used for further study on the reaction between PEI-epi and rosin. The spectrum of rosin is too complicated to give a clear indication to the possible chemical reaction. Therefore, a fatty acid, sodium oleate, was used instead. Sodium oleate has a similar carboxyl group but the structure is much simpler than that of rosin. It should be noted that this study indicated sodium oleate could also size the paper in neutral to alkaline conditions in the presence of PEI-epi (results are not shown in this paper). Sodium oleate and PEI-epi were mixed in water (without fibers) at different weight ratios at room temperature. The mixture was then vacuum-dried to remove the water. The dried mixture was then heated at 100 °C for 20 min to promote reaction. The spectra from the reaction product of sodium oleate and PEI-epi are shown in Fig. 10. When the spectrum of the mixture is compared with that of sodium oleate and PEI-epi, a new peak appears at around 1734 cm. This peak is very likely from the ester bond formed between azetidinium group on the PEI-epi and the carboxyl group in sodium oleate. At a fixed dosage of sodium oleate, the peak increased in absorbance with the increasing amount of PEI-epi. A large amount of PEI-epi results in a more completely reacted product.

It can be concluded from FTIR study that a reaction did occur between PEI-epi and sodium oleate during the curing process in the absence of fibers. However, more study is needed to understand the interaction mechanism between PEI-epi rosin during paper-sizing development, particularly to determine whether the reaction is to form amide through the secondary amine groups in PEI-epi and fatty acid or is to form ester through the azetidinium group and fatty acid.

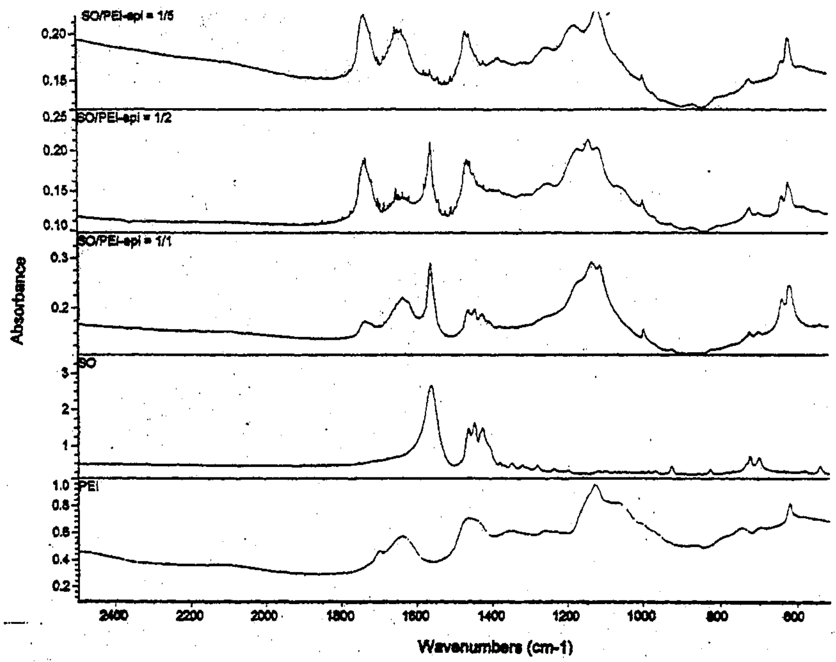


Figure 10. FTIR Spectra of PEI-epi and Sodium Oleate at Different Ratios After Curing.

Sizing reversion of PEI-epi/Dispersed Rosin System

It was noted in this study that the sizing degree of cured handsheets significantly decreased after they were left at room temperature for a few days. This is surprising because if the PEI/epi formed covalent bonds with rosin, these bonds should be strong and should not degrade easily without adding other chemicals. Furthermore, the chemical reaction in dry condition is usually slower than in a solution (molecules movement is limited in dry condition). This phenomenon suggests that the real role of PEI/epi in this particular system needs to be further studied.

CONCLUSION

PEI-epi is a potential mordant for rosin sizing at neutral to slightly alkaline pH conditions, with the highest sizing level obtained at neutral pH. This sizing process is applicable to both bleached and unbleached furnishes. Sizing results are affected by the process conditions, such as rosin/PEI-epi ratio, temperature, and reaction time. The sizing level is comparable with the traditional alum-rosin system at the same added amount of rosin. PEI-epi/dispersed rosin sizing provides significant gains in wet-tensile strength, which may be an additional advantage for certain grades of paper. It is likely that a chemical reaction happens between PEI-epi and rosin, but more study is needed to get further evidence about this reaction. The sizing reversion observed in this study needs to be solved in the future study.

LITERATURE CITED

1. Wortley, B., "Bonding with Polyaluminum Chloride Makes Neutral Rosin Sizing Possible", *Pulp and Paper*, 64(11):131 (1990).
2. Liu, J., "Sizing with Rosin and Alum at Neutral pH", *Paper Technology*, 34(8):20 (1993).
3. Liu, J., " Comparison of Alum and PAC Neutral Sizing System", *Paper Technology*, 36(5):20 (1995).
4. Colasurdo, A. R., " Rosin Sizing at Neutral pH", 1990 Neutral/Alkaline Papermaking Short Course, TAPPI Press, Atlanta, GA, 71-78.
5. Biermann, J., " Rosin Sizing with Polyamine Mordants from pH 3 to 10", *Tappi J.*, 75(5):166 (1992).
6. Wu, Z., Chen, S. and Tanaka, H., "Effects of Polyamine Structure on Rosin Sizing under Neutral Papermaking Conditions", *J. Appl. Polymer Sci.*, 65:2159 (1997).

7. Zhang, J. and Biermann, J., " Neutral to Alkaline Rosin Soap Sizing with Metal Ions and Polyethyleneimine as Mordants", *Tappi J,* 78(4):155 (1995).
8. Isogai, A., "Mechanism of Paper Sizing by Cationic Emulsion of Fatty Acid Anhydrides", *J. Pulp Paper Sci.*, 25(6):211 (1999).
9. Kitaoka, T., Isogai, A. and Onabe, F., "Sizing Mechanism of Emulsion Rosin Sizing-Alum System, Part 3. Solid-state ^{13}C-NMR Analysis of Handsheets Prepared by ^{13}C-labeled Fatty Acid-Alum Systems", *Nordic Pulp Paper Res. J.,* 12(3):182 (1997).
10. Kitaoka, T., Isogai, A. and Onabe, F., "Sizing Mechanism of Emulsion Rosin Sizing-Alum System, Part 2. Structure of rosin size components in the paper sheet", *Nordic Pulp Paper Res. J.,* 12(1):26 (1997).
11. Isogai, A., Taniguchi, R. and Onabe, F., "Sizing Mechanism of Alkylketene Dimers, Part 4. Effect of AKD and Ketone in Emulsions on Sizing", *Nordic Pulp Paper Res. J.,* 9(1):44 (1995).
12. Linderström, T. and Söderberg, G., "On the Mechanism of Sizing with Alkylketene Dimer, Part I: Studies on the Amount of Alkylketene Dimer Required for Sizing Different Pulps", *Nordic Pulp Paper Res. J.,* 1(1):26 (1986).
13. Roberts, G. and Garner, N., "The Mechanism of Alkyl Ketene Dimer Sizing of Paper, Part 1", *Tappi J.* 68(4):118 (1985).
14. Ödberg, L., Linderström T., Liederg, B. and Gustravsson, J., "Evidence for β-ketoester Formation during the Sizing of Paper with Alkylketene Dimers", *Tappi J.* 70(4):135 (1987).
15. Bottorf, K., "AKD Sizing Mechanism: A More Definitive Description", *Tappi J.,* 77(4):105 (1994).
16. Roberts, J., *Paper Chemistry*, 107, Blackie Academic & Professional, 1992.
17. Marton, J., "Wet-End Factors Influence the Choice of Size", *1987 Sizing Short Course*, 53-62.